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STUDIES OF REACTION GEOMETRY IN OXIDATION AND REDUCTION
OF THE ALKALINE SILVER ELECTRODE

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ABSTRACT

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In reduction of the alkaline AgO electrode the reaction occurs preferentially in regions where the oxide layer is thinnest. Surface roughness and shallow pitting do not cause perceptible effect upon the reaction. A depth discontinuity in the AgO, however, results in preferential reactions beneath the thin region.

The reaction on discharge of AgO plates started at the grid in our experiments (current density 0.23-6.4 ma/cm²).

In oxidation of sintered silver plates at 3 ma/cm² the reaction started always at the solution sintered interface and proceeded toward the grid.

In constant potential oxidation of sintered silver plates a current minimum is consistently observed soon after the start of oxidation. Investigation of this is being continued.

Author

PART I

INTRODUCTION

In charge and discharge of the silver (II) oxide electrode, control of the current density is important in prediction of life and capacity of the electrode. Experiments at Jet Propulsion Laboratory (Ref. 1) showed that in the discharge of commercial AgO plates there were frequently found regions of preferential reaction. Since these regions were often observed to represent only a very small fraction of the total area of the plate the actual current densities were estimated to be as much as one hundred times that value calculated from total current and gross surface area. The present study was started, therefore, to investigate the reactions of the alkaline silver cell in an effort to determine what characteristics of the plate cause variations in electrolytic reactivity.

PART II

EXPERIMENTS

A. Sources of Electrodes

Commercial plates consisting of pressed AgO on Ag grids were used for exploratory experiments. Inasmuch as these plates had surface and thickness characteristics which we could not control, we used these only in early experiments to give indication of the effect of various observable irregularities.

AgO was prepared by the method of Bailer (Ref. 2). This was dried at room temperature in a vacuum desiccator for a period of 48 hours and was stored in a closed container. All samples used analyzed 97% or higher AgO, in terms of its oxidizing capacity.

The chemically prepared AgO was pressed onto Ag grid (Exmet 5 Ag 10-4/10 or equivalent) in dies under a pressure of 40,000 p.s.i. (see Figure I). No binder was used in the AgO since electrolytic reaction could be affected by such a binder, and since heat treatment of the plate to remove the binder causes decomposition of the AgO (Ref. 1). Ag₂O was prepared from reagent grade AgNO₃ and NaOH. This was pressed at 40,000 p.s.i. on grids of Ag. Again no binder was used. Plates consisting of sintered silver on silver grid were obtained from commercial sources. These plates were 0.4 mm thick and were constructed with the grid centered in the sintered silver.

B. Preparation of Plates for Experiments

Electrical contact to the plates was made by soldered connection. This connection and the wire were completely covered with alkali-

resistant Tygon coating (Van Waters & Rogers, Series "K"). An ordinary rosin-core solder was used in some experiments but was replaced with thermal junction free solder to ensure that no rosin was dispersing through the sintered silver plates by capillary action. To eliminate edge effects to the extent possible, the plates used in charge and discharge experiments were prepared oversize and then masked with Tygon coating to the size wanted. Most plates were prepared at 2.5 cm on an edge and masked to a 1 cm square. Weight loss of the quantity of Tygon coating used in masking was found to be less than 1 mg in the length of time of the longest experiments. Plates having surface irregularities were prepared by the use of die faces having the reverse irregularities.

For example, plates with rough surfaces were pressed with a die face of aluminum which had been abraded with emery cloth. The roughness of the plate was controlled by the grade of abrasive material. Acid etching of the die face was used for introducing very slight unevenness to the plate surface. Sharp discontinuities in oxide thickness were made by the use of an overlay of the appropriate thickness on half the die face.

C. Instruments

A Leeds and Northrup No. 7960 coulometric analyzer was used as the constant current source for the experiments reported here. This instrument has output rates of 0.643, 6.43, and 64.3 ma. The output was checked periodically by measurement of the potential drop across a standard resistor with a potentiometer (see Figure II).

A Hewlett-Packard Model 881AX power supply was used for constant potential experiments. The potential is continuously variable from 0 to 100 volts and the current is similarly variable from 0 to

1 ampere. In constant current operation resistance changes from 9,000 to 10 ohms caused variations of less than 2 ma in a total current of 100 ma. Sudden large percentage changes in resistance (10% or greater) cause momentary small changes in current but the instrument compensated for these changes in about 3 seconds to restore the current to its pre-set value. We have not encountered such sudden changes in the resistance or potential of cells. Changes in external resistance from 5 to 1000 ohms cause voltage change of less than 40 mv.

During constant potential experiments the current which passed through the cell was recorded directly with a Leeds and Northrup Speedomax H recorder. The recorder measured the potential drop across a 0.10 ohm (50 watt) resistor which was in series with the cell. Our concern with this resistor was that its power capacity be high enough that it not heat and fluctuate in resistance. The 10% accuracy was considered to be sufficient, since the resistor in conjunction with the recorder served to monitor current and yielded good relative values. This resulted in a very slight variation in the potential applied to the cell. In a typical run the current decreased from 20 ma to 0.2 ma. Thus, the potential drop across the 0.1 ohm resistor dropped from 2 mv to 0.02 mv. Since the output potential of the power supply was 1.80 ± 0.02 v in the experiments reported here, the potential applied to the cell was not significantly affected by the change in potential drop across the resistor. The output potential of the power supply was monitored by means of a 100 megohm, internal resistance vacuum tube voltmeter (Kintel 202B) (see Figure III).

PART III

RESULTS AND DISCUSSION

A. Effect of Surface Irregularities

1. Roughened and pitted surfaces: Examination of a partially reduced plate of either AgO or Ag_2O by means of a 30 power binocular microscope showed no effect of a roughened surface upon reaction geometry in constant current discharge at 2 ma/cm^2 . The depth of surface roughening was of the order of 0.02 mm on a plate of total thickness 0.8 mm. The reaction (as is discussed below) invariably started in our experiments at the grid of either AgO or Ag_2O electrodes and an electrode with its surface partially roughened and partially smooth did not react preferentially under one or the other.

2. Discontinuities in depth of grid below oxide surface: The reaction occurs preferentially where the oxide layer is thinnest. Grooves and depressions of 0.1 mm and 0.2 mm in a 0.8 mm plate resulted consistently in preferential reaction beneath the thin area. After having been partially reduced the plates were examined with a 30 power binocular microscope for surface effects. The plate was then carefully broken so that it could be examined in cross section. Cutting the plate tended to smear the cut section until regions of reduction and non-reduction were indistinct. An abrupt change is readily apparent in the region of the grid beneath a variation in thickness of the oxides. This appears to be a straight-forward resistance effect, and emphasizes the danger in estimating cell behavior from current densities if there are any fissures, grooves, or fractures in the oxide layer. Relatively

few of the commercial plates which we have examined have been free from such features. Experiments are now being performed in which discharge of irregular plates is done at constant potential.

B. Locus of Reaction

1. AgO or Ag₂O plates: The reduction of AgO and oxidation or reduction of Ag₂O invariably occurred at the grid in our experiments (apparent current density on plate surface was kept at 2 ma/cm²). The reaction proceeded in an approximately radial manner from the wire of the grid until the region about the grid was all reacted. The reaction continued then toward the surface in an apparently uniform manner if the surface was smooth (see Figure IV).

2. Sintered silver plates: In the oxidation of silver plates at constant apparent-current-densities in the range from 0.3 to 6.4 ma/cm² the reaction was found to start always at the surface of the electrode and proceed toward the grid in a very uniform manner (see Figure V). A detailed study of the progress of reaction in the region of the grid when almost all of the sintered silver has been oxidized to Ag₂O has been started. We cannot draw sound conclusions from these experiments yet.

C. Current Variations in Constant Potential Charge of Sintered Silver Plates

Figures VI and VII show current variation (as plotted by potential drop across a fixed resistor) during the initial period of a constant potential--1.80 v.--charge of 2 cm² (1 cm² on each side) sintered silver plates. The increase in current is observed consistently in such experiments but the total number of coulombs varies appreciably. Figures VI and VII show the extremes we have encountered in the quantity of charge

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before the current rise appears. Graphical integration of the two plots from the start of the charge experiment to the minimum of the curve yields 0.350 coulombs and 3.56 coulombs for Figures VI and VII, respectively. If it is assumed that these quantities of electricity were effective in oxidizing silver to Ag_2O and that this oxidation proceeded from the surface uniformly, the depths of oxidation would be 2.90×10^{-5} cm and 2.97×10^{-4} cm, respectively. The silver was sintered, so the microscopic surface area was vastly greater than the gross area of 2 cm^2 .

PART IV

PROPOSED WORK

- A. A detailed determination of the geometry of reaction during the final stages of oxidation of Ag constant current is being made. It is our attempt to determine how the oxidation proceeds as the grid is approached.
- B. Investigation is being made of the current rise which we observe in the constant potential oxidation of Ag to AgO. We are attempting to find correlation between the extent of change of the plate when the rise appears and the extent of oxidation of the silver. We will make use of silver plates of very different surface areas in this attempt.
- C. We propose to determine current efficiency at constant current as a function of state of change of plates. The problem of obtaining satisfactory analysis of a plate which may consist of Ag, Ag_2O and AgO is one which has not been solved to our satisfaction. We are working on this problem.

REFERENCES

1. J.P.L. Technical Report 32-535 (1963). Discharge Behavior of the AgO - Ag Electrode.
2. Bailer, J. C., Jr., Inorganic Syntheses, IV, p. 12, McGraw-Hill, New York, New York, 1953.

DIE FOR PRESSING SILVER OXIDE PLATES

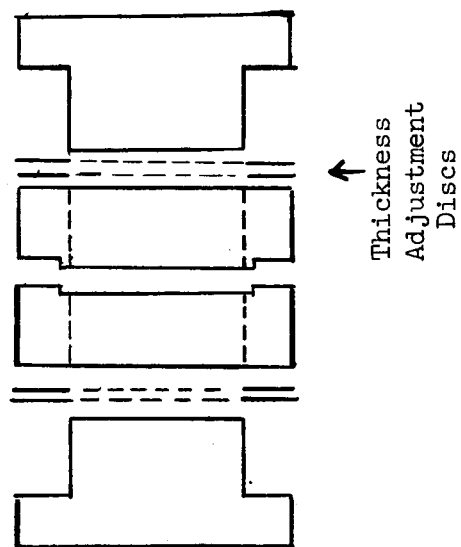


Figure I

BLOCK DIAGRAM FOR CONSTANT CURRENT PROCESSES

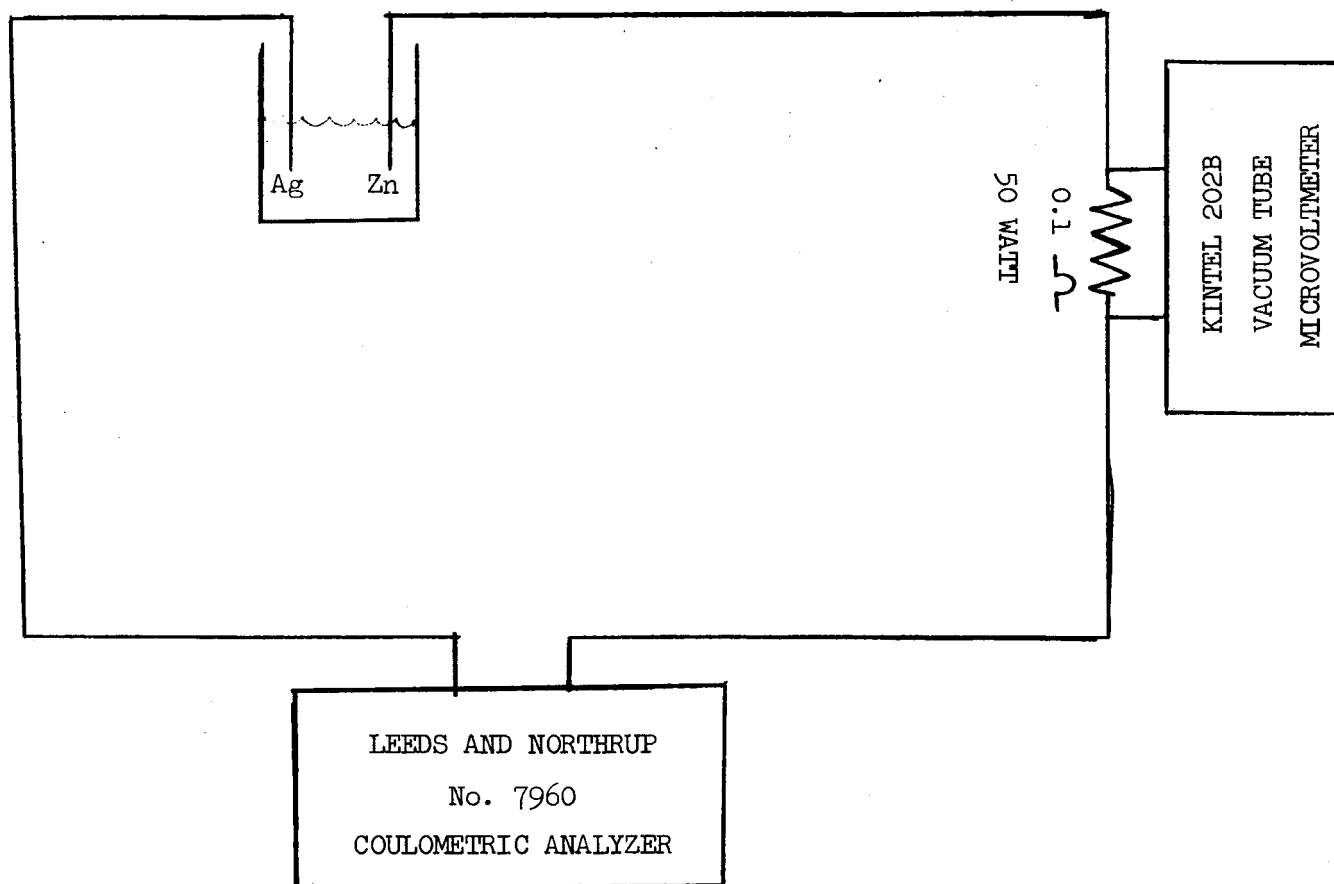


Figure II

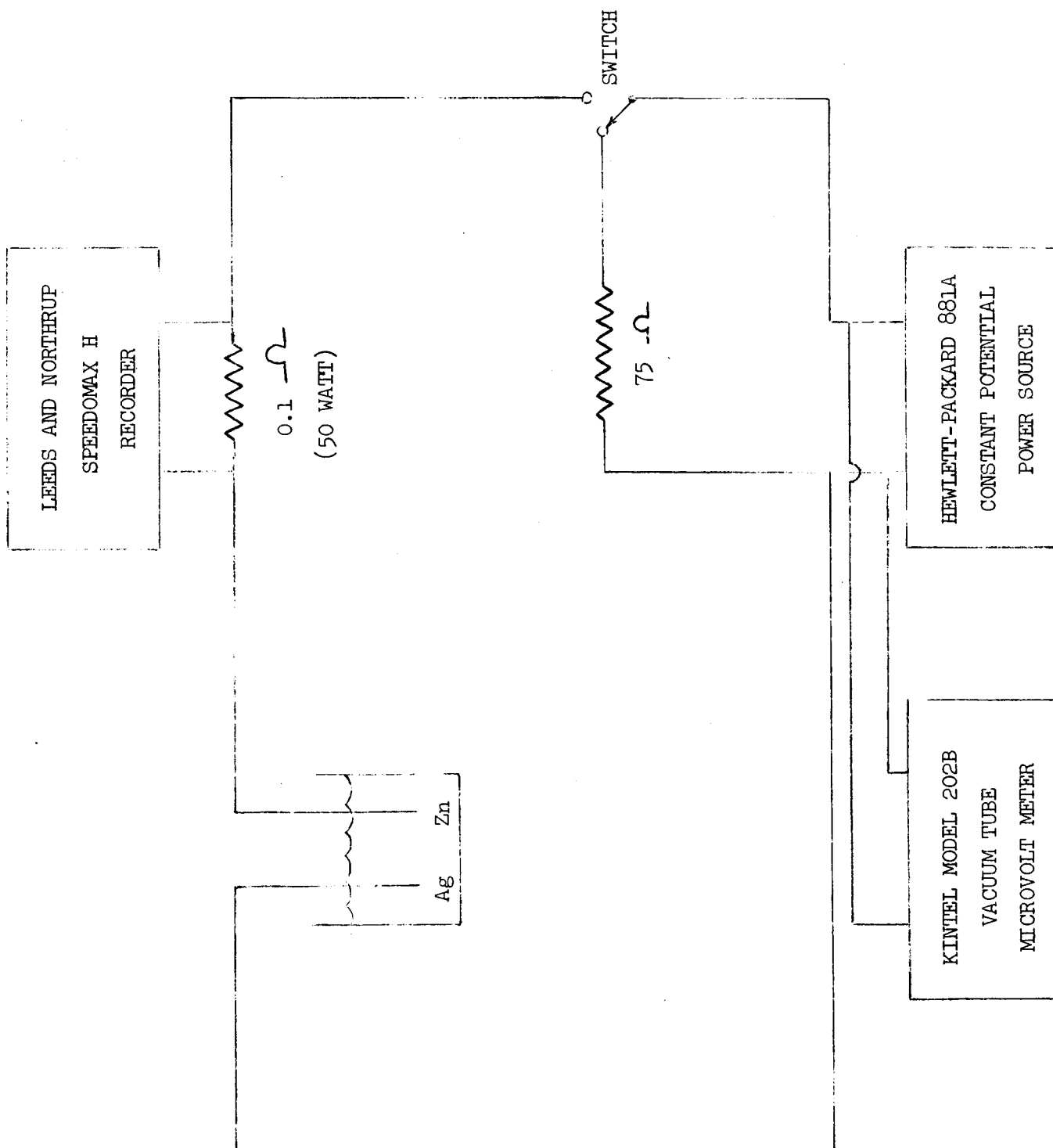


Figure III

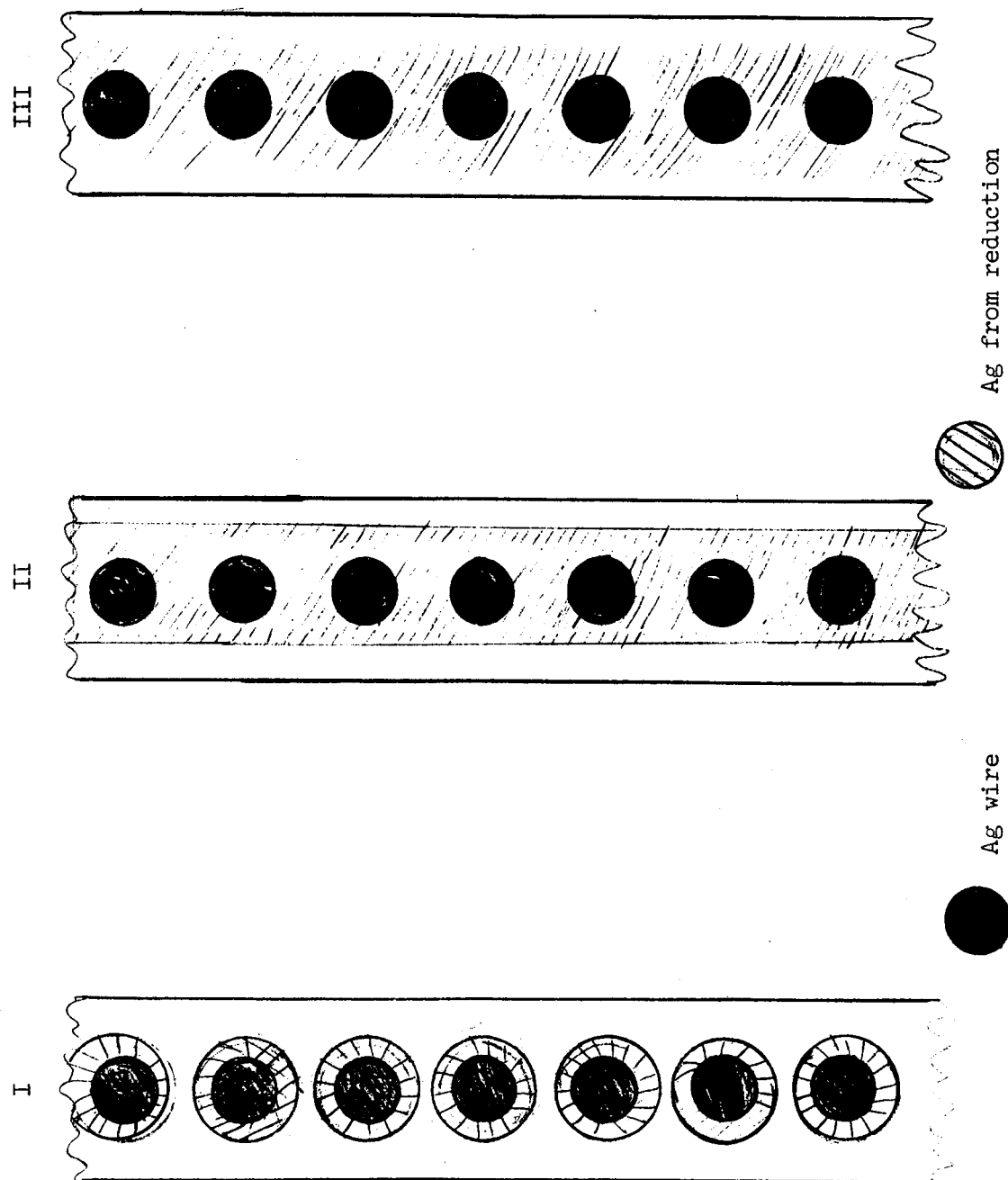
REDUCTION OF Ag_2O AT CONSTANT CURRENT

Figure IV

 Ag_2O

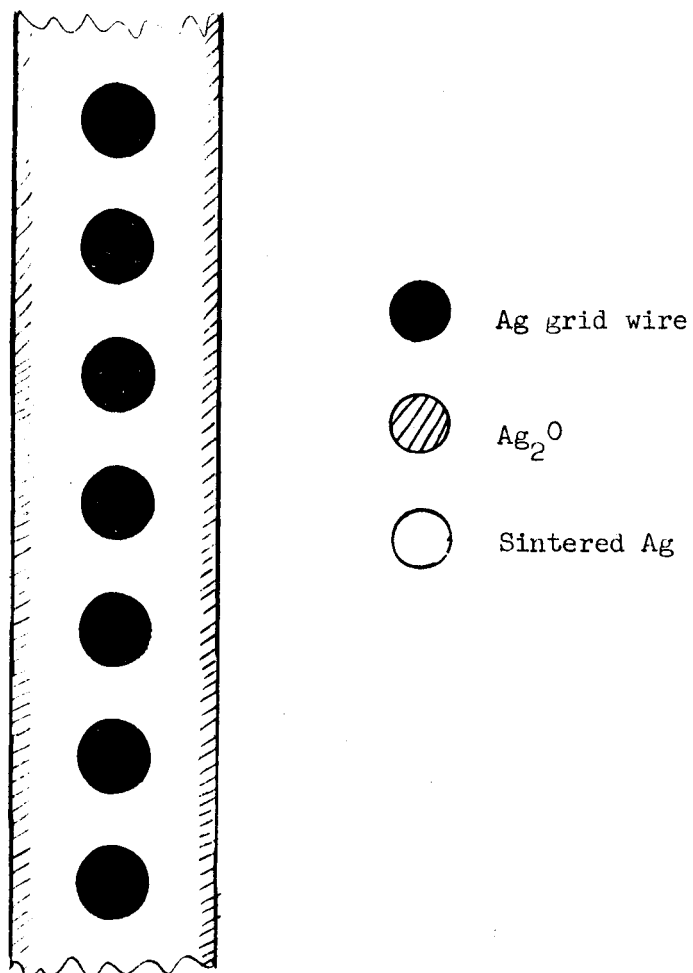
OXIDATION OF SINTERED SILVER TO Ag_2O 

Figure V

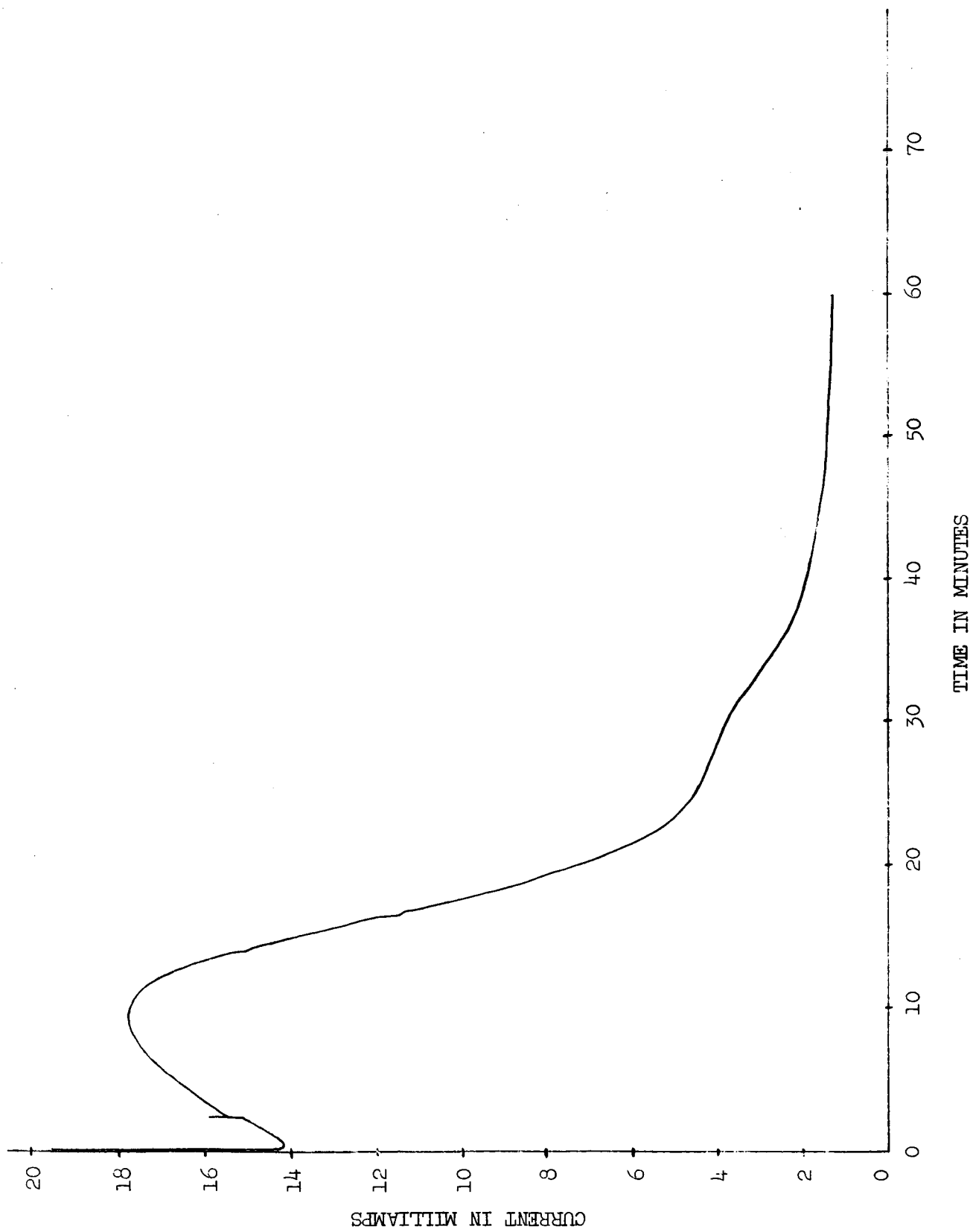


Figure VI

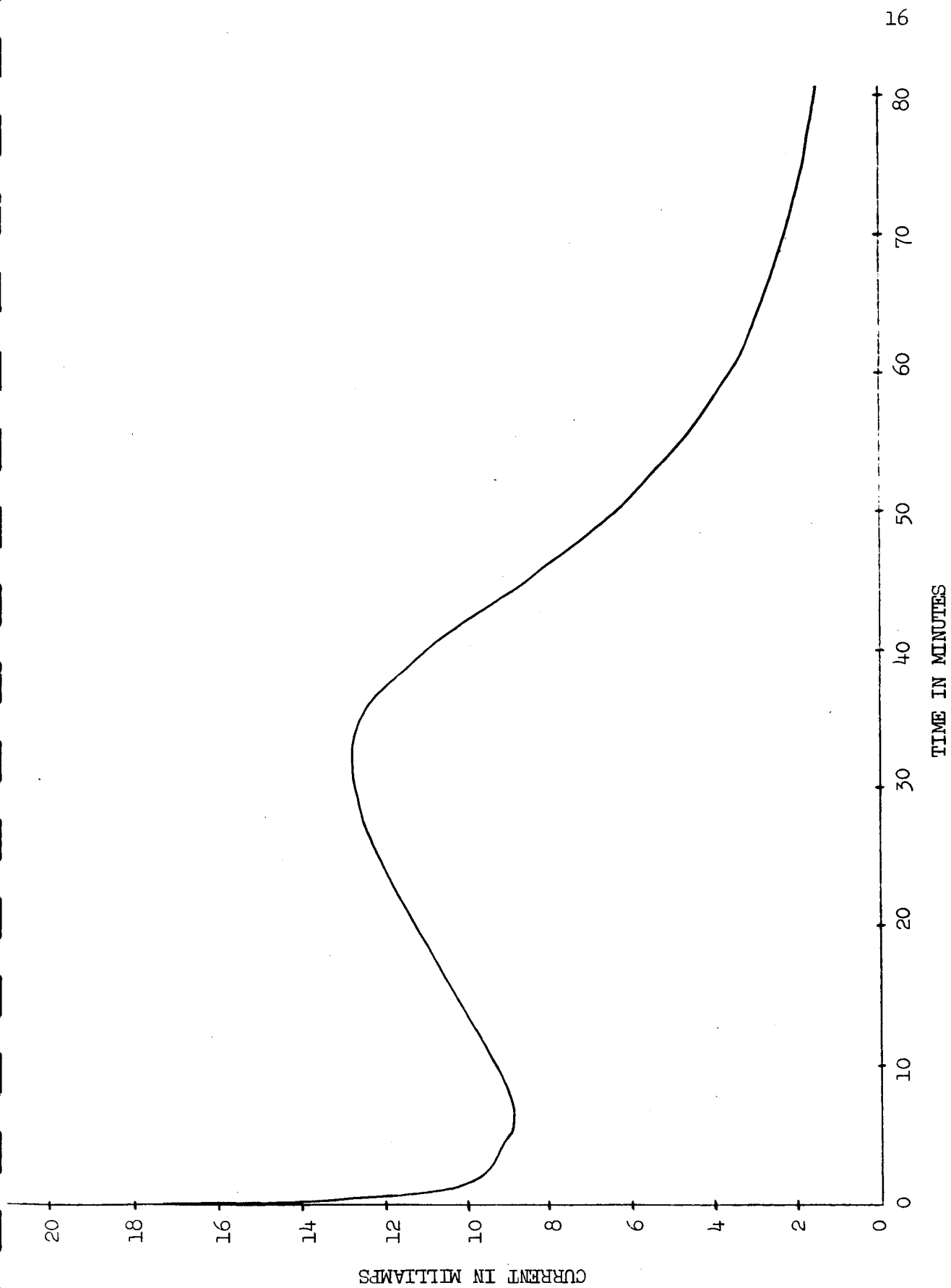


Figure VII